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SPECIFIC HEAT OF POLYTETRAFLUOROETHYLENE AND POLYCHLOROTRIFLUOROETHYLENE WITHIN THE TEMPERATURE RANGE 2.5–20 K

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Low-temperature specific heat measurements on bulk technical polymer samples (polytetrafluoroethylene and polychlorotrifluoroethylene) were carried out between 2.5 and 20 K. In these experimental investigations a heat pulse method and an adiabatic vacuum calorimeter were used.

The low-temperature specific heats of polytetrafluoroethylene (T_4) and polychlorotrifluoroethylene (T_3) have not been studied in sufficient detail [1–15]. The extrapolation of the experimental values at 20 K down to 4 K by means of the Debye-model is inadmissible [5]. Thus, investigations of the thermal properties giving the necessary physical quantities and constants for cryogenic design of these highly crystalline polymers are quite important.

In the present work, calorimetric measurements on the bulk polymer samples were made in the range 2.5–20 K. The length and diameter of the samples did not surpass 50 mm and 12 mm, respectively. By using a shield in a vacuum calorimeter [16], entirely adiabatic conditions of operation were ensured. The cooling of the calorimeter, as well as that of the sample and the shield, was effected with a mechanical heat switch [17]. The heat capacity was derived from a well-known relation between the increase of the sample temperature ($\Delta T \sim 10^{-2}\,T$) and the amount of heat supplied to the sample by a 650 Ω heater, consisting of 0.050 mm diameter constantan wire. This heater gives heat impulses lasting 40 seconds. The temperatures of the samples and the shield were measured by 300Ω Allen-Bradley resistors. The calibration of these resistors was performed using a germanium (NIG) substandard. The time for establishment of the heat equilibrium was a few seconds at 2.5 K, and about 15 minutes at 20 K.

Experimental

The temperature-dependence of the specific heat is presented in Fig. 1 for polychlorotrifluoroethylene, and in Fig. 2 for polytetrafluoroethylene. The values of C/T^3 for T_3 at 4 K ($C/T^3 = 0.057$ mj/gK^4) obtained by Reese and Tucker [3] from

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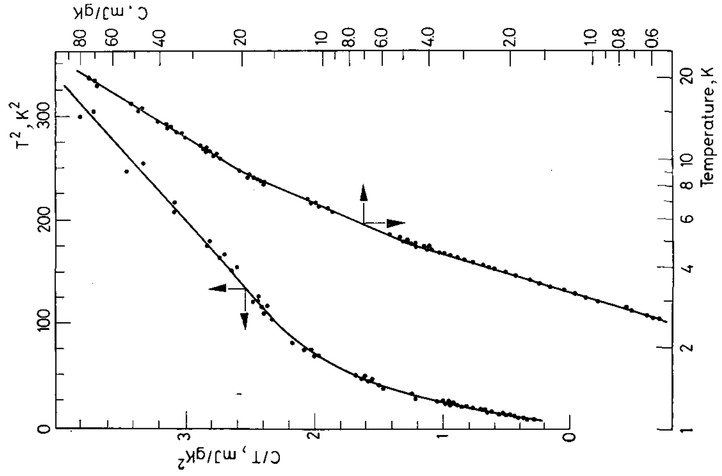
T², K²
0
100
200
300
C/T, mJ/gK²
0
1
2
3
C, mJ/gK
80
60
40
20
10
8.0
6.0
4.0
2.0
1.0
0.8
0.6
Temperature, K
1
2
4
6
8
10
20

Fig. 2

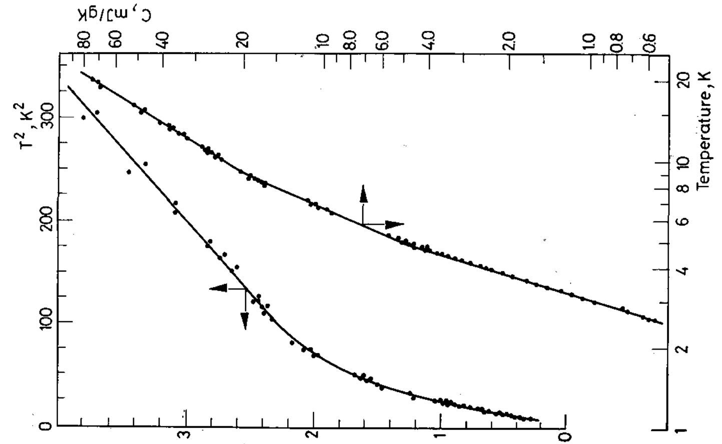
T², K²
0
100
200
300
C/T, mJ/gK²
0
1
2
3
C, mJ/gK
80
60
40
20
10
8.0
6.0
4.0
2.0
1.0
0.8
0.6
Temperature, K
1
2
4
6
8
10
20

Fig. 1

indirect measurements (the heat capacity was calculated from the thermal conductivity and thermal time constant) are higher than the values of C/T^3 ($C/T^3 = 0.048$ mj/gK^4) obtained in our heat pulse calorimetric measurements. There are no specific heat measurements for this polymer in the temperature range 4–20 K with which the present results can be compared.

A comparison of the results of the specific heat measurements of different authors [1–11] for T_4 is made in Table 1. We can draw the following conclusions from Table 1 and Fig. 2:

1. In the temperature range 15–20 K our results are in reasonable agreement with the data of Furukawa *et al.* [7].

2. For the first time the present measurements supply a $T^{2.5}$ dependence of the specific heat at 4.9–9 K for T_4 ($C = 0.0856\ T^{2.5}$ mj/gK) and at 4.3–6.7 K for

Table 1

A comparison of results of different authors [3, 4, 7, 8, 9, 10, 11] and review articles [1, 2, 5, 6]

Direct calorimetric measurements						Indirect measurements		Modulus measurements		Acoustic measurements		Our measurements	
7		4		8		3		9		10, 11			
T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$	T/K	C/$\frac{mJ}{gK}$
		0.3–1.3	$0.035T^3$										
				1.4–4.2	$0.040T^3$	1.0–4.0	$0.0454T^3$	1.0–4.0	$0.0450T^3$	1.0–4.0	$0.0281T^3$	2.5–4.9	$0.0369T^3$
												4.9–9.0	$0.0856T^{2.5}$,
15	47.2											15	46.9
20	76.7											20	75.8

T_3 ($C = 0.0967\ T^{2.5}$ mj/gK). This is in very good agreement with the theoretical models [13–15]. Unfortunately, in the given temperature ranges for these two polymers there are no experimental data of other authors for comparison with ours.

3. The experimental results for the specific heat at 2.5–4.9 K follow a T^3 law, as shown by Noer *et al.* [8], Reese and Tucker [3, 9], and Scott and Giles [4]. However, these low-temperature calorimetric values of C/T^3 for T_4 as well as those for T_3 are larger by more than 50% compared to accoustic values [10] and give $\Theta_D^{T_4} = 102$ K and $\Theta_D^{T_3} = 70$ K.The reason for this discrepancy is unknown[11] for the time being. Some authors [12] point out that such a phenomenon may be provoked by the existence of low-frequency localized modes.

A correction for the parasitic heat flows and the heat capacities of the additions to the sample was introduced into the programme calculation of the experimental results according to the calibration curve of the calorimeter with Osborn copper. The reproducibility of the experimental data was about ±1% at 20 K.

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Résumé — On a effectué des mesures de chaleur spécifique à basse température, entre 2.5 et 20 K, sur des échantillons de polymères techniques en vrac (polytétrafluoroéthylène et polychlorotrifluoroéthylène), à l'aide d'une méthode par impulsions de chaleur et d'un calorimètre adiabatique sous vide.

ZUSAMMENFASSUNG — Messungen der spezifischen Wärme bei niedrigen Temperaturen wurden an technischen Polymerproben "alla rinfusa" (Polytetrafluoräthylen und Polychlortrifluoräthylen) zwischen 2.5 und 20 K durchgeführt. Bei diesen experimentellen Untersuchungen wurde eine Wärmepulsierungsmethode und ein adiabatisches Vakuumcalorimeter eingesetzt.

Резюме — Проведены низкотемпературные измерения удельной теплоемкости технических полимерных образцов (политетрафторэтилен и полихлортрифторэтилен) между 2.5 и 20 К. В проведенных исследованиях использовали метод теплового импульса и адиабатический вакуумный калориметр.